Investigation of Some Hydroxamic Acids by Thermometric Titrimetry

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Introduction

Hydroxamic acids, generally RCON(OH)R′, are interesting and versatile compounds which have quite a distinguished history of involvement in chemical reactions. H. Lossen (11), in 1869, reported that the reaction between diethyl oxalate and hydroxylamine yielded an acidic compound which he named oxalohydroxamic acid. The reaction discovered by Lossen has since been found to be quite general and forms the basis for a qualitative test for esters (12).

The acids are found also in nature and are known to have interesting biological properties (16); indeed, they are by-products of a number of biochemical reactions (2). The qualitative test for esters is based upon formation of hydroxamic acids and their complexing properties with iron (III) (12). It has been conjectured that they could play an important role in biochemical processes involving transport of trace metals throughout living systems. Indeed, their complexing action is not limited to iron (III) but encompasses many other metals: cobalt, copper, zinc to name only three (14). Hydroxamic acids also occur as the radiolytic degradation products of solvents and diluents used in the extraction processes for the recovery of uranium and plutonium from irradiated fuels (1, 13).

It is essential that these somewhat obscure but clearly important compounds be determined accurately in a variety of matrices, and, although a number of methods do exist (3), it was considered to be appropriate to investigate them through the use of thermometric titrimetry (8-10). This method is not only a sensitive analytical technique but also has the potential of producing data of fundamental imortance: enthalpies, Gibbs free energy, entropies and equilibrium constants (5). It is the object of this paper to report on such studies undertaken with these compounds.

Method and Apparatus

Thermometric titrimetry is a simple technique relying upon a universal property of all chemical reactions for endpoint detection: the evolution or absorption of heat. Generally, during the reaction, heat is absorbed or evolved and when this process ceases the end of the reaction is signaled, the latter may be detected using a simple thermistor circuit. The complete apparatus is shown in Figure 1, and consists of a small Dewar vessel of about 15 ml. capacity fitted with a cover suitably bored for a mechanical stirrer, a resistive heater, a thermistor heat sensor and a reagent delivery tube. The thermistor forms one arm of a Wheatstones' bridge circuit the output of which is connected to an amplifier and chart recorder. The titrant is delivered through a small diameter Teflon tube connected to a syringe driven by a synchronous motor. The Dewar vessel is usually immersed in a waterbath thermostated at 25°C. so that the experiments may be conducted at a constant known temperature. More details concerning available apparatus and reaction conditions are given in reference (5).

The method used for the investigation was akin to a conventional titration except that the titrant was added continuously at a constant rate, and the temperature of the stirred solution was monitored continuously by the thermistor circuit. Figure 2 shows the type of data normally produced by titration of a weak the curve

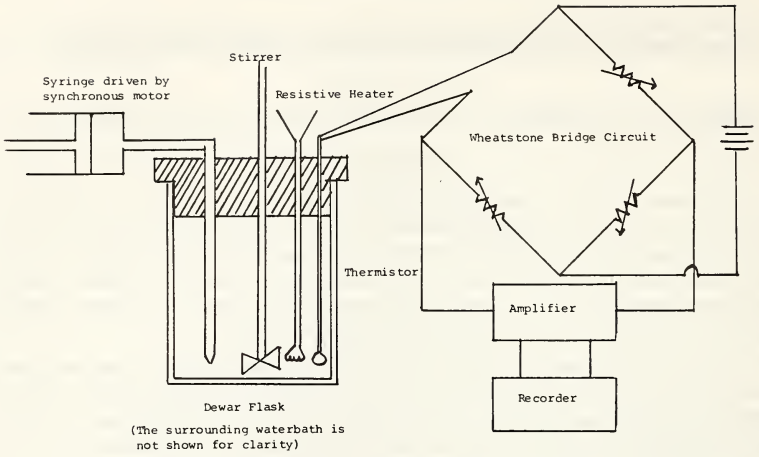

FIGURE 1: *The Complete Apparatus*

indicating little or no temperature rise prior to the titration; point B is where addition of titrant starts; point C is where the reaction concludes and is usually determined as the intersection of BC and CD. Finally, CD is the post-titration portion of the curve and usually corresponds to an excess of reagent. The diagram is read by extrapolating DC to F and then erecting a line at B perpendicular to the volume axis to intersect DC at F, the height, BF, being the temperature increase of the solution at zero volume increase (△ T). The distance, B′E′, along the volume axis corresponds to the volume of titrant consumed by any analyte present during the titration (△ V).

In order to obtain enthalpy values for any reaction conducted one more measurement has to be made: the heat capacity of the solution (C). This is accomplished by creating a known potential difference (V_H) across a small accurately known resistance (R_H) and measuring the time for which the current flows (t

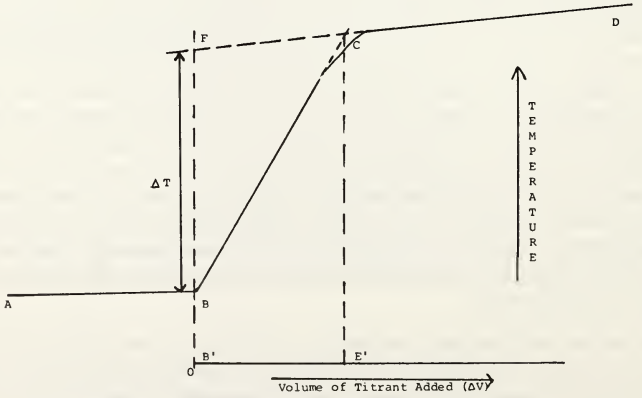

FIGURE 2: *A Typical Thermometric Titration Curve*

seconds). This heat flow will then correspond to a definite rise in temperature ($\triangle T_c$) which may be measured. the calculation is made with the following formula:

$$C = \frac{V_H^2 t}{4{\cdot}184 R_H \triangle T_c} \text{ calories}$$

The enthalpy of the reaction may then be calculated by applying the following equation:

$$\triangle H = \frac{C \triangle T}{\triangle n} \text{ calories}$$

where $\triangle n$ is the number of moles of analyte involved in the reaction.

Experimental

Reagents: Acetohydroxamic acid and salicylhydroxamic acid were purchased (Aldrich Chemical Co.) and recrystallized twice from an ethanol-water mixture; N-phenylbenzohydroxamic acid and benzohydroxamic acid were synthesized and purified by the usual methods (4, 7). All melting points were corrected and found to tally with those available in the literature. The sodium hydroxide used was prepared to be about 0.1M and carbonate-free by a suitable method (15) and standardized in the usual fashion (15). All the water used was distilled, deionized and carbonate-free.

Method: Solutions of the acids in water were made containing between 1.0 and 6.0 milimoles per litre and aliquots were loaded into the Dewar flask using a calibrated pipette. The flask was attached to the stopper and then the whole immersed in an external constant temperature waterbath. After thermal equilibrium of the flask and contents was attained, sodium hydroxide solution was introduced using a syringe pump and the reaction monitored by the thermistor circuit. The experiment was repeated several times for each acid at different concentrations and reagent flow rates.

TABLE 1: *Thermodynamic Data for Several Hydroxamic Acids*

Function* / Acid	$\triangle H°$ neut. (Kcal/mol)	pK_a Ref. (6)	$\triangle H°$ dep. (Kcal/mol)	$\triangle G°$ dep. (Kcal/mol)	$\triangle S°$ dep. (Cal/mol/K)
N-phenylbenzohydroxamic acid	-(11.5 ± 0.2)	8.35 ± 0.02	(2.02 ± 0.02)	(11.39 ± 0.03)	-30
Benzohydroxamic acid	-(7.33 ± 0.05)	8.87 ± 0.04	(6.19 ± 0.08)	(12.10 ± 0.05)	-20
Salicylhydroxamic acid	-(8.40 ± 0.06)	7.51 ± 0.05	(5.12 ± 0.03)	(10.25 ± 0.07)	-17
Acetohydroxamic acid	-(8.50 ± 0.05)	9.41 ± 0.01	(5.02 ± 0.03)	(12.84 ± 0.01)	-26

* The items used in the table are as follows:
$\triangle H°_{neut.}$ = standard enthalpy of neutralisation.
$\triangle H°_{dep.}$ = standard enthalpy of deprotonation.
$\triangle G°_{dep.}$ = standard Gibbs free energy of deprotonation.
$\triangle S°_{dep.}$ = standard entropy of deprotonation.

Results and Conclusions

The molar heat of neutralization was calculated for each of the hydroxamic acids and these, coupled with potentiometrically determined acid dissociation constants (16) were used to calculate other valuable thermodynamic data of fundamental importance at a temperature of 298K for the reaction

$$HA \rightleftharpoons H^+ + A^-,$$

and are embodied in Table 1. A brief consideration of this data shows no apparent trend in the values although N-substitution may affect the value for $\triangle H°_{dep}$, the standard enthalpy of deprotonation. However, there is too little data to draw any conclusions as yet and more information must be gathered.

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